



The selective catalytic reduction of N₂O with CH₄ on Na-MOR and Na-MFI exchanged with copper, cobalt or manganese

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ABSTRACT

Cu-MOR, Cu-MFI, Co-MOR, Co-MFI and Mn-MFI were prepared by ion-exchange of Na-MOR or Na-MFI. On all samples, the catalytic activity for N₂O decomposition, CH₄ + N₂O, CH₄ + O₂, and for the selective catalytic reduction (SCR) of N₂O in the presence of O₂ was studied in a flow apparatus with GC analysis of reactants and products.

Extensively exchanged Cu-MOR and Cu-MFI were active for N₂O decomposition. Cu-MOR and Cu-MFI exchanged at about 20% were much less active. All Co-MOR and Co-MFI catalysts, irrespective of the exchange-extent, were active for the same reaction. Mn-MFI was nearly inactive up to 773 K. All catalysts were active for CH₄ + N₂O. Cu-MOR and Cu-MFI were active for CH₄ + O₂, whereas Co-MOR, Co-MFI and Mn-MFI were much less active for this reaction. Irrespective of the exchange extent, Cu-MOR, Cu-MFI, Co-MOR, and Co-MFI were active for the SCR of N₂O with CH₄. Conversely, Mn-MFI was not active for this reaction. Turnover frequency was slightly higher for the various reactions on Me-MFI (Me = Cu or Co) than for the corresponding reactions on Me-MOR.

We conclude that on Cu- and Co-zeolites, the SCR of N₂O with CH₄ consists of two nearly independent reactions: CH₄ + N₂O prevails at high temperature (673–773 K), and CH₄ + O₂ at lower temperature. The two reactions involve different catalytically active oxygen species: CH₄ + O₂ involves a molecular form, and CH₄ + N₂O a monoatomic form, arising from N₂O. Because Co-MOR and Co-MFI are also active for the SCR of NO_x, we suggest that these materials are promising catalysts for the simultaneous SCR of N₂O and NO_x with CH₄.

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1. Introduction

Uhde's proprietary EnviNOx[®] process performs the tail-gas abatement of N₂O and NO_x over iron containing zeolite catalysts. In cooperation with Süd-Chemie, Uhde has developed special iron-exchanged zeolite catalysts for use in the EnviNOx[®] process [1]. For EnviNOx[®], Hevia and Pérez-Ramírez evaluated a possible variant for the low-temperature abatement process (<700 K), in which NH₃ selectively reduces NO_x, and CH₄ selectively reduces N₂O. For this purpose, these investigators ran activity tests with mixtures N₂O, O₂, NO, NH₃, and CH₄ at different temperatures and partial pressures over steam-activated FeZSM-5 [2].

Iron-containing MFI zeolites are active for N₂O abatement with various hydrocarbons (CH₄, C₂H₆, C₂H₄, C₂H₂, C₃H₈, C₃H₄) [3] and with CH₄, CO, or CH₄ + CO mixtures [4]. These catalysts and analogous iron-containing catalysts are poorly active for N₂O decomposition [4,5] and inactive for NO_x abatement with CH₄ in

the presence of excess O₂ [6]. A drawback with the iron-containing zeolites is the CO formation during N₂O or NO_x abatement using hydrocarbon reducing agents [3,7–9].

Co-MOR and Co-MFI [5,10–12] and extensively exchanged Cu-MOR and Cu-MFI [10,11,13] are strongly active for N₂O decomposition. Co-MOR, Co-MFI and Mn-MFI are active and selective for NO_x abatement with CH₄ in the presence of excess O₂. On cobalt and manganese zeolites, in the selective catalytic reduction of NO with CH₄ in the presence of excess O₂, no CO formed [14–16]. This result differed from that on iron-containing zeolites, on which CO formed [3,7–9]. These findings prompted us to study the catalytic activity of Cu-MOR, Cu-MFI, Co-MOR, Co-MFI and Mn-MFI for the selective catalytic reduction of N₂O with CH₄ in the presence of O₂ (SCR of N₂O with CH₄). The catalysts we tested were nearly identical to or portions of those we have previously characterized by FTIR, using CO or NO as probe molecules, and volumetric adsorption of CO [11,16,17]. In preliminary experiments, we checked that the activity for the N₂O decomposition of Cu-MOR, Cu-MFI, Co-MOR, and Co-MFI matched that of the analogous samples investigated previously for this reaction [11], and we measured the activity of Mn-MFI for the same reaction. The primary aim of the investigation

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Table 1

Copper-, cobalt-, or manganese-exchanged MOR or MFI: starting materials, analytical copper, cobalt, manganese, and sodium amounts.

Starting materials	Catalysts	Na ⁺ /Al	2Me ²⁺ /Al ^a
Na-MOR-9.2		1.05	
	Cu–Na-MOR-9.2-20	0.82	0.20
	Cu–Na-MOR-9.2-100	0.36	1.05
	Co–Na-MOR-9.2-23	0.79	0.23
	Co–Na-MOR-9.2-104	0.28	1.04
Na-MFI-11.9		1.00	
	Cu–Na-MFI-11.9-22		0.22
	Cu–Na-MFI-11.9-93	0.17	0.93
	Co–Na-MFI-11.9-15	0.79	0.15
	Co–Na-MFI-11.9-92	0.05	0.92
	Mn–Na-MFI-11.9-53	0.49	0.53

^a Me²⁺/Al is Cu²⁺/Al, Co²⁺/Al, or Mn²⁺/Al, depending on the catalyst.

was to gain a basic understanding of (i) the SCR of N₂O with CH₄ and (ii) the selectivity dependence on temperature, with Cu-MOR, Cu-MFI, Co-MOR, Co-MFI and Mn-MFI as catalysts. To this aim, we compared the activity of these samples for N₂O decomposition with that of the same samples for CH₄ + N₂O, CH₄ + O₂, and SCR of N₂O with CH₄.

Because Co-MOR and Co-MFI [14,15], and Mn-MFI [16] are active for the SCR of NO_x with CH₄, we also investigated which of these materials might be potential catalysts for the simultaneous SCR of N₂O and NO_x using CH₄ as the only reducing agent.

2. Experimental

2.1. Catalysts

Cu-, Co-, Mn-exchanged zeolites and the starting materials for their preparation are listed in Table 1. Na-MOR (Si/Al = 9.2), and Na-MFI (Si/Al = 11.9), kindly supplied by Tosoh Corporation, were used for ion exchange. In Na-MOR and in Na-MFI samples, the analytical Na content equalled the Al content calculated from the analytical Si/Al ratio given by the supplier. Copper, cobalt or manganese containing samples were ion-exchanged at 350 K by contacting a weighted amount of zeolite (MOR or MFI) with an aqueous solution of acetates of copper, cobalt, or manganese, as required. To obtain extensively exchanged samples, up to three exchange procedures were run in sequence. After the exchange procedure, samples were thoroughly washed with distilled water, and dried overnight at 383 K.

The sodium, the copper, the cobalt, and the manganese content of wet samples (equilibrated at ca. 79% relative humidity over a saturated solution of NH₄Cl) were determined by atomic absorption (Varian SpectraAA-30), and expressed as Na⁺/Al and 2Me²⁺/Al ratios, where Me is the transition metal ion exchanged (Cu, Co, or Mn). Exchanged samples are labeled as Me–Na-ZEO-*a*-*b*, where Me specifies the transition metal ion exchanged (Cu, Co or Mn), Na specifies that the zeolite used in the preparation was in the sodic form, ZEO specifies the type of zeolite (MOR or MFI), *a* is the Si/Al ratio value, and *b* is the analytical metal ion exchange percentage, calculated assuming that one Me corresponded to two Al atoms (Table 1).

2.2. Catalytic experiments

The catalytic activity was measured in a flow apparatus at atmospheric pressure. The apparatus included a feeding section where four gas streams (He, 3% N₂O in He, 1.5% CH₄ in He, 15% O₂ in He) were regulated by means of independent mass flow controllers (MKS mod. 1259, driven by a four-channel unit MKS mod. 247 c) and mixed in a glass ampoule before entering the reactor.

Table 2

Catalytic reactions and feed mixture composition.

Reaction	Composition mixture/ppm (v/v)
N ₂ O → N ₂ + 1/2O ₂	N ₂ O = 4000
CH ₄ + 4N ₂ O → 4N ₂ + CO ₂ + 2H ₂ O (CH ₄ + 3N ₂ O → 3N ₂ + CO + 2H ₂ O) ^a	CH ₄ :N ₂ O = 1000:4000
CH ₄ + 2O ₂ → CO ₂ + 2H ₂ O (CH ₄ + 3/2O ₂ → CO + 2H ₂ O) ^a	CH ₄ :O ₂ = 1000:2000 (or 20,000)
(CH ₄ + 2N ₂ O + O ₂ → 2N ₂ + CO ₂ + 2H ₂ O) ^a	CH ₄ :N ₂ O:O ₂ = 1000:4000:2000 (or 20,000)
(CH ₄ + N ₂ O + O ₂ → N ₂ + CO + 2H ₂ O) ^a	

^a Because on our catalysts no CO formed in any of the experiments, and CH₄ + N₂O + O₂ did not react according to the 1:2:1 stoichiometry, the reactions in parentheses will not be considered.

Gas mixtures were purchased from RIVOIRA and used without further purification. The reactor was made of silica with an internal sintered frit of about 12 mm diameter supporting the powdered catalyst (0.1 g). In all experiments, reactants and products were analyzed by gas-chromatography. The gas chromatograph (Varian Micro-GC CP-4900) was equipped with two columns: (i) 10 m Molsieve 5A BF, for detecting O₂, N₂, and CO, and (ii) 10 m Poraplot Q, for detecting CH₄, CO₂, and N₂O. All possible reactions are listed in Table 2. No CO formed in any of the experiments. All experiments yielded satisfactory nitrogen, carbon and oxygen balances. For the SCR of N₂O with CH₄, the stoichiometric ratios (N₂O molecules reacted)/(CH₄ molecules reacted) and (O₂ molecules reacted)/(CH₄ molecules reacted) markedly changed as a function of temperature,

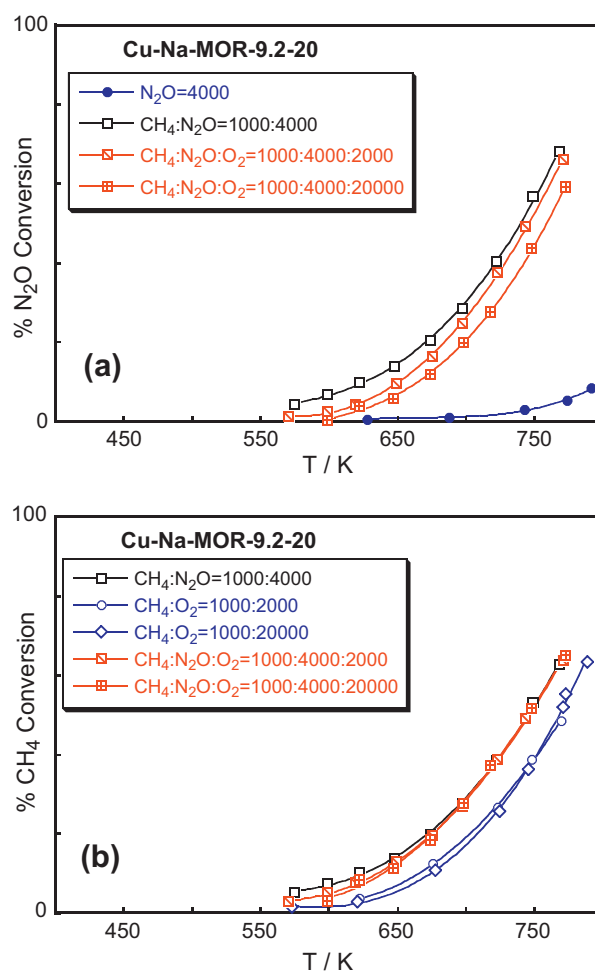


Fig. 1. Percent N₂O conversion (Section a) and percent CH₄ conversion (Section b), as a function of temperature on Cu–Na-MOR-9.2-20, reactions as indicated.

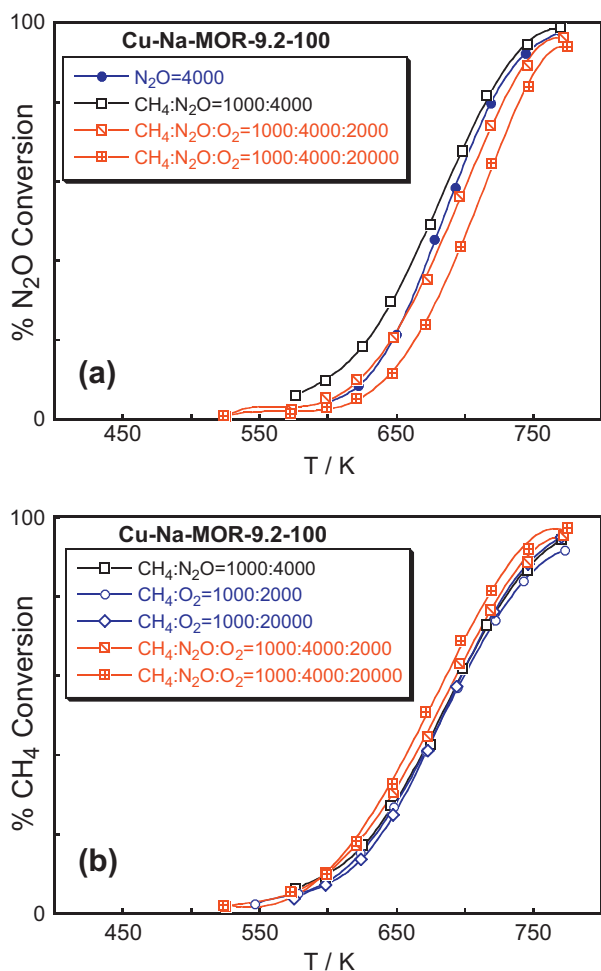


Fig. 2. Percent N₂O conversion (Section a) and percent CH₄ conversion (Section b), as a function of temperature on Cu–Na–MOR-9.2-100, reactions as indicated.

showing that on our catalysts CH₄ + N₂O + O₂ did not react according to the 1:2:1 stoichiometry (Table 2). The stoichiometric ratio (N₂O molecules reacted)/(CH₄ molecules reacted) will hereafter be referred to as N₂O/CH₄ and that (O₂ molecules reacted)/(CH₄ molecules reacted) as O₂/CH₄.

A fresh portion of catalyst was treated in a flow of 2.5% O₂/He mixture (100 cm³ min^{−1}), while the reactor was heated from room temperature to 773 K in about 45 min and then isothermally at 773 K for 90 min. After this treatment, the reactor was bypassed and the temperature adjusted to the desired value. Catalysis was run by contacting catalysts with mixtures of various composition (Table 2). The reaction temperature was changed at random without intermediate activation treatment. For all reactions, all catalysts were stable as a function of the time on stream, throughout experiments lasting up to about 25 h. The total flow rate was maintained at 50 cm³ STP/min, and space velocity (GHSV) was 15,000 h^{−1}, based on the apparent sample density of 0.5 g cm^{−3}.

Percent N₂O, CH₄, or O₂ conversion was calculated from molecules consumed/molecules injected. Turnover frequency, $N_{\text{N}_2\text{O}}$ or N_{CH_4} (N/molecules s^{−1} atom^{−1}), was calculated as $N = R/[L]$, where R is the specific velocity $R_{\text{N}_2\text{O}}$ or R_{CH_4} (R/molecules s^{−1} g^{−1}), and $[L]$ is the concentration of active sites ($[L]/\text{atoms g}^{-1}$). To calculate N , we assumed that all exchanged transition metal ions were active, $[L] = [\text{Me}^{2+}]_{\text{tot}}$.

In the SCR of N₂O with CH₄, the CH₄ selectivity for N₂O was calculated as $S_{\text{N}_2\text{O}} = (\text{CH}_4 \text{ molecules reacted with N}_2\text{O})/(\text{CH}_4 \text{ molecules reacted with N}_2\text{O} + \text{CH}_4 \text{ molecules reacted with O}_2)$,

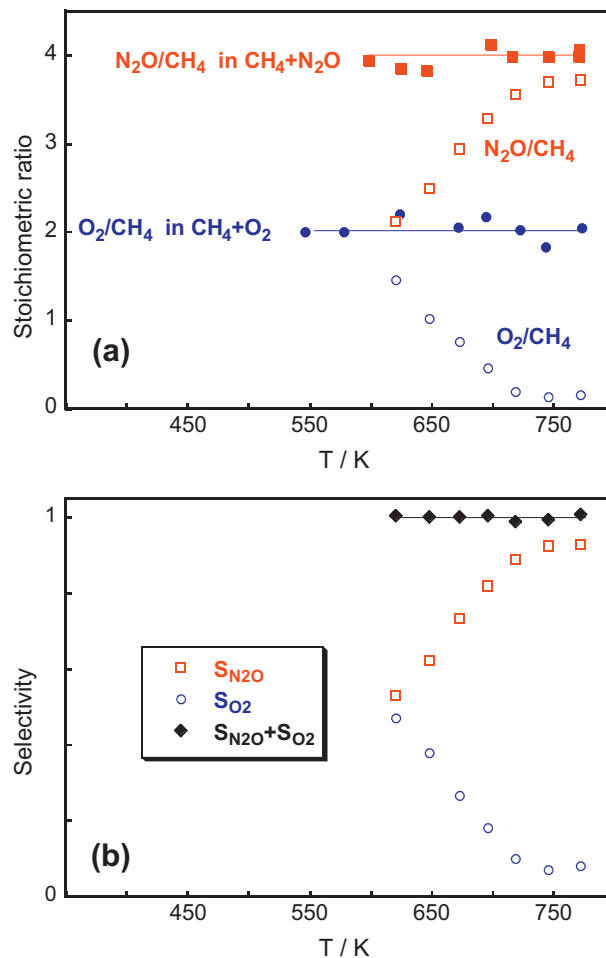


Fig. 3. Stoichiometric ratio for CH₄ + N₂O, and CH₄ + O₂ and CH₄ + N₂O + O₂ reactions (Section a) and selectivities in the CH₄ + N₂O + O₂ reaction (Section b). Section a: stoichiometric ratio of reacted molecules as a function of temperature for CH₄ + N₂O, and CH₄ + O₂ (closed points, reaction as indicated), and for CH₄ + N₂O + O₂ (open points, CH₄:N₂O:O₂ = 1000:4000:2000). Section b: selectivities, $S_{\text{N}_2\text{O}}$, S_{O_2} , and $S_{\text{N}_2\text{O}} + S_{\text{O}_2}$, in the CH₄ + N₂O + O₂ reaction (CH₄:N₂O:O₂ = 1000:4000:2000), as a function of temperature. $S_{\text{N}_2\text{O}} = (\text{CH}_4 \text{ molecules reacted with N}_2\text{O})/(\text{CH}_4 \text{ molecules reacted with N}_2\text{O} + \text{CH}_4 \text{ molecules reacted with O}_2)$; $S_{\text{O}_2} = (\text{CH}_4 \text{ molecules reacted with O}_2)/(\text{CH}_4 \text{ molecules reacted with N}_2\text{O} + \text{CH}_4 \text{ molecules reacted with O}_2)$. Catalyst: Cu–Na–MOR-9.2-100.

where CH₄ molecules reacted with N₂O were determined from N₂O molecules consumed, and CH₄ molecules reacted with O₂ were determined from O₂ molecules consumed. In the same reaction, we also calculated CH₄ selectivity for O₂ as $S_{\text{O}_2} = (\text{CH}_4 \text{ molecules reacted with O}_2)/(\text{CH}_4 \text{ molecules reacted with N}_2\text{O} + \text{CH}_4 \text{ molecules reacted with O}_2)$.

3. Results and discussion

3.1. The catalytic activity of Cu–Na–MOR and Cu–Na–MFI

On Cu–Na–MOR-9.2-20 and Cu–Na–MOR-9.2-100, the N₂O conversion in the N₂O decomposition matched that we previously measured on the corresponding Cu–Na–MOR samples [11]. Conversion was very low on Cu–Na–MOR-9.2-20, and was much higher on Cu–Na–MOR-9.2-100. This conversion dependence resembled that we have previously observed on Cu–Na–MOR and Cu–Na–MFI [11] and it agreed with that reported by Smeets et al. on Cu–MFI [13].

On the Cu–Na–MOR-9.2-20 sample, the N₂O conversion in CH₄ + N₂O, and in the SCR of N₂O with CH₄ was much higher than in N₂O decomposition (Fig 1a). On the same sample, the CH₄

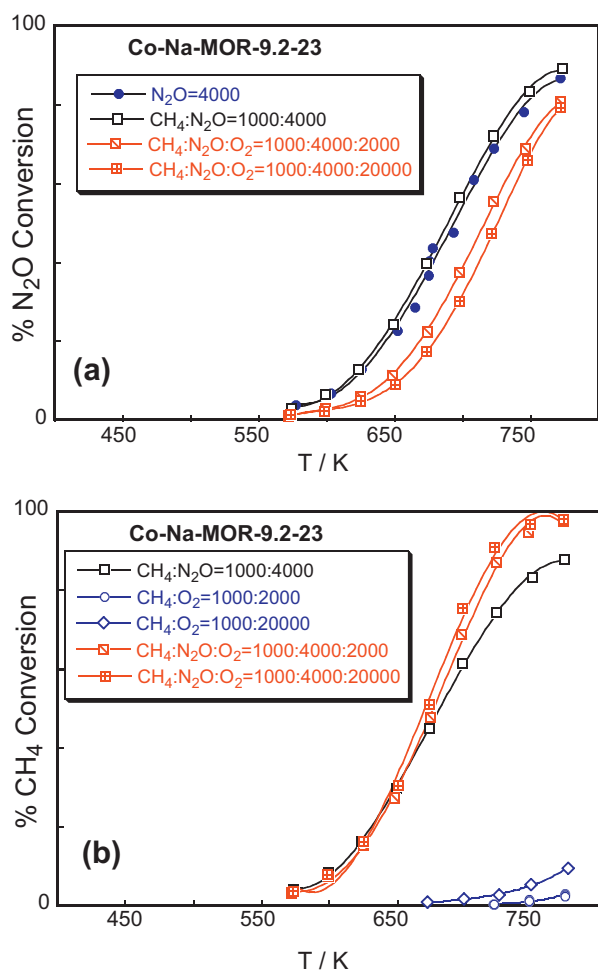


Fig. 4. Percent N₂O conversion (Section a) and percent CH₄ conversion (Section b), as a function of temperature on Co-Na-MOR-9.2-23, reactions as indicated.

conversion was roughly the same in CH₄ + N₂O and in the SCR of N₂O with CH₄, and it was slightly higher in these two reactions than in CH₄ + O₂ (Fig. 1b). The results on Cu-Na-MOR-9.2-100 sample were analogous to those observed on Cu-Na-MOR-9.2-20. An important difference between Cu-Na-MOR-9.2-20 and Cu-Na-MOR-9.2-100 was that on Cu-Na-MOR-9.2-100 N₂O conversion in N₂O decomposition differed little from that measured in CH₄ + N₂O and in the SCR of N₂O with CH₄ (Fig. 2a and b). Namely, CH₄ favoured N₂O abatement to a greater extent on Cu-Na-MOR-9.2-20 than on Cu-Na-MOR-9.2-100.

On Cu-Na-MOR, in the SCR of N₂O with CH₄, the N₂O/CH₄ ratio markedly increased with temperature reaching a value close to the stoichiometric ratio in the reaction CH₄ + 4N₂O → 4N₂ + CO₂ + 2H₂O. In parallel, the O₂/CH₄ ratio progressively and markedly decreased with temperature starting from a value close to the stoichiometric ratio in the reaction CH₄ + 2O₂ → CO₂ + 2H₂O (Fig. 3a). In agreement, the selectivity S_{N₂O} markedly increased with temperature, reaching a value close to 1 at 773 K, and the selectivity S_{O₂} markedly decreased with temperature, reaching a value close to zero at the same temperature. At all temperatures, the sum S_{N₂O} + S_{O₂} was close to 1 (Fig. 3b).

For all reactions, N₂O decomposition, CH₄ + N₂O, CH₄ + O₂, and CH₄ + N₂O + O₂, the results we obtained on Cu-Na-MFI were analogous to those obtained on Cu-Na-MOR. Specifically, the catalytic behaviour of Cu-Na-MFI-11.9-22 (data not shown) was

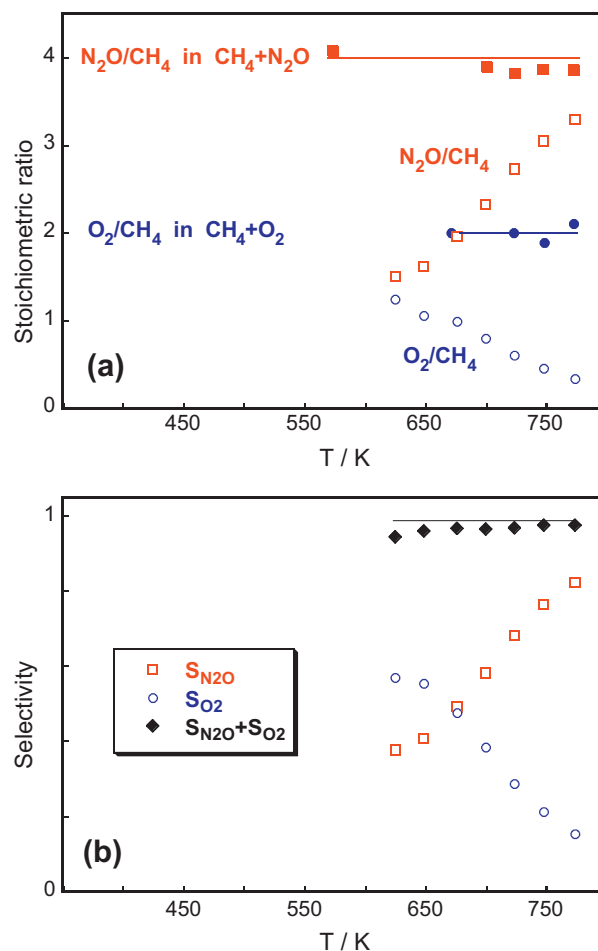


Fig. 5. Stoichiometric ratio for CH₄ + N₂O, and CH₄ + O₂ and CH₄ + N₂O + O₂ reactions (Section a) and selectivities in the CH₄ + N₂O + O₂ reaction (Section b). Section a: stoichiometric ratio of reacted molecules as a function of temperature for CH₄ + N₂O, and CH₄ + O₂ (closed points, reaction as indicated), and for CH₄ + N₂O + O₂ (open points, CH₄:N₂O:O₂ = 1000:4000:2000). Section b: selectivities, S_{N₂O}, S_{O₂}, and S_{N₂O} + S_{O₂}, in the CH₄ + N₂O + O₂ reaction (CH₄:N₂O:O₂ = 1000:4000:2000), as a function of temperature. S_{N₂O} = (CH₄ molecules reacted with N₂O)/(CH₄ molecules reacted with N₂O + CH₄ molecules reacted with O₂); S_{O₂} = (CH₄ molecules reacted with O₂)/(CH₄ molecules reacted with N₂O + CH₄ molecules reacted with O₂). Catalyst: Co-Na-MOR-9.2-104.

analogous to that of Cu-Na-MOR-9.2-20 and the catalytic behaviour of Cu-Na-MFI-11.9-93 (data not shown) was analogous to that of Cu-Na-MOR-9.2-100. The turnover frequency for the various reactions on Cu-Na-MFI was slightly higher than that for the corresponding reactions on Cu-Na-MOR (data not shown).

Collectively, these findings strongly suggest that on Cu-Na-MOR and Cu-Na-MFI the SCR of N₂O with CH₄ consists of two independent reactions, taking place on the same copper containing active site: (i) CH₄ + 4N₂O → 4N₂ + CO₂ + 2H₂O and (ii) CH₄ + 2O₂ → CO₂ + 2H₂O.

3.2. The catalytic activity of Co-Na-MOR and Co-Na-MFI

On Co-Na-MOR-9.2-23 and Co-Na-MOR-9.2-104, N₂O conversion in the N₂O decomposition equalled that we previously measured on the corresponding Co-Na-MOR samples [11]. Namely, R_{N₂O} velocity (R_{N₂O}/molecules s⁻¹ atom⁻¹, data not shown) increased proportionally to the cobalt content, as we previously observed on Co-Na-MOR samples with Co-exchange percentage from 6 to 104% [11].

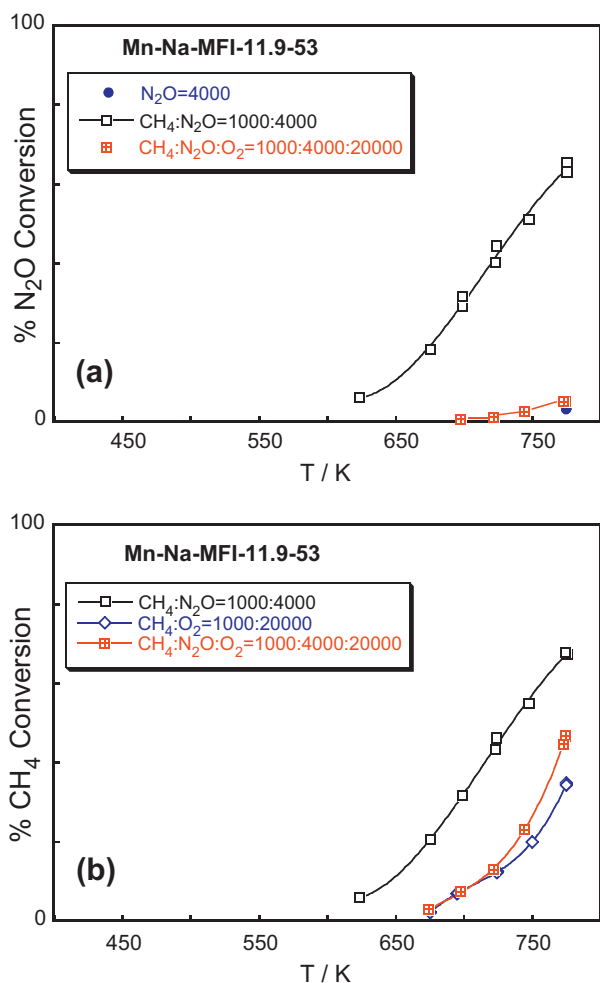


Fig. 6. Percent N₂O conversion (Section a) and percent CH₄ conversion (Section b), as a function of temperature on Mn–Na–MFI-11.9-53, reactions as indicated.

On Co–Na–MOR-9.2-23, the N₂O conversion in N₂O decomposition equalled that in CH₄ + N₂O, and was slightly higher than that in CH₄ + N₂O + O₂ (Fig. 4a). On the same sample, the CH₄ conversion was roughly the same in CH₄ + N₂O, and CH₄ + N₂O + O₂, and it was much higher in these two reactions than that in CH₄ + O₂ (Fig. 4b). The results on Co–Na–MOR-9.2-104 sample were analogous to those on Co–Na–MOR-9.2-23 (data not shown).

On Co–Na–MOR, in the SCR of N₂O with CH₄, the N₂O/CH₄ ratio markedly increased with temperature reaching a value close to the stoichiometric ratio in the reaction CH₄ + 4N₂O → 4N₂ + CO₂ + 2H₂O. In parallel, the O₂/CH₄ ratio markedly decreased with temperature starting from a value close to the stoichiometric ratio in the reaction CH₄ + 2O₂ → CO₂ + 2H₂O (Fig. 5a). In agreement, the selectivity S_{N₂O} markedly increased with temperature, reaching a value close to 0.8 at 773 K, and the selectivity S_{O₂} markedly decreased with temperature, reaching a value close to 0.2 at the same temperature. At all temperatures, the sum S_{N₂O} + S_{O₂} was close to 1 (Fig. 5b).

For all reactions, the catalytic behaviour of Co–Na–MFI was analogous to that of Co–Na–MOR, and the turnover frequency on Co–Na–MFI was slightly higher than that for the corresponding reactions on Co–Na–MOR (data not shown).

All these findings strongly suggest that the SCR of N₂O with CH₄ on Co–Na–MOR and Co–Na–MFI consists of two independent reactions, taking place on cobalt containing active site: CH₄ + 4N₂O → 4N₂ + CO₂ + 2H₂O and CH₄ + 2O₂ → CO₂ + 2H₂O.

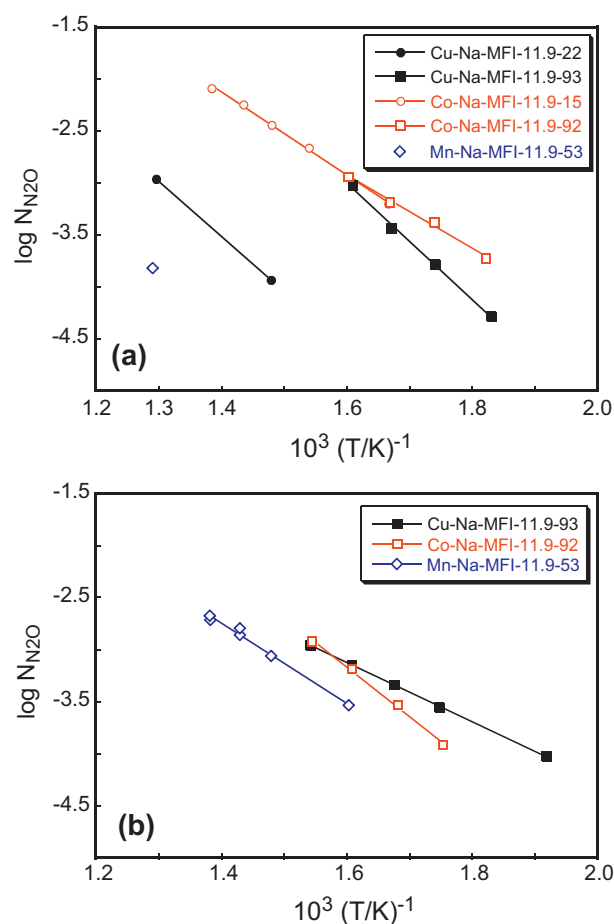


Fig. 7. Arrhenius plots, log N_{N_2O} vs. $1/T(N_{N_2O}/\text{molecules s}^{-1} \text{ atom}^{-1})$, for the N₂O decomposition (Section a) and for CH₄ + N₂O (Section b) on Me–Na–MFI catalysts (Me = Cu, Co, or Mn), as indicated.

3.3. The catalytic activity of Mn–Na–MFI

On Mn–Na–MFI-11.9-53, the N₂O conversion in the N₂O decomposition was very low, resulting $\leq 5\%$ at 773 K. This result agrees with that previously reported by Li and Armor on an extensively exchanged Mn–MFI catalyst [5].

On Mn–Na–MFI-11.9-53, the N₂O conversion in CH₄ + N₂O was much higher than in N₂O decomposition and in CH₄ + N₂O + O₂ (Fig. 6a). The CH₄ conversion in CH₄ + N₂O + O₂ and that in CH₄ + O₂ was roughly the same and it was substantially lower than that in CH₄ + N₂O (Fig. 6b).

On this sample, in the SCR of N₂O with CH₄, the N₂O/CH₄ ratio was close to zero at all temperatures. In parallel, the O₂/CH₄ ratio was close to 2. In agreement, the selectivity S_{N₂O} was nearly zero at all temperature, whereas the selectivity S_{O₂} was close to 1 at all temperatures (data not shown).

3.4. A comparison of the catalytic activity of Me–Na–MFI (Me = Cu, Co, or Mn)

In N₂O decomposition, the comparison among the various Me–Na–MFI shows that N_{N_2O} (N₂O molecules converted s⁻¹ atom⁻¹) on Co–Na–MFI and Cu–Na–MFI was much higher than that on Mn–Na–MFI (Fig. 7a). The fact that N_{N_2O} on Cu–Na–MFI-11.9-93 was higher than that on Cu–Na–MFI-11.9-22 (Fig. 7a) has been already discussed in a previous paper from our group [11].

Conversely, in CH₄ + N₂O, the comparison shows that N_{N_2O} changed little among the various Me–Na–MFI (Fig. 7b).

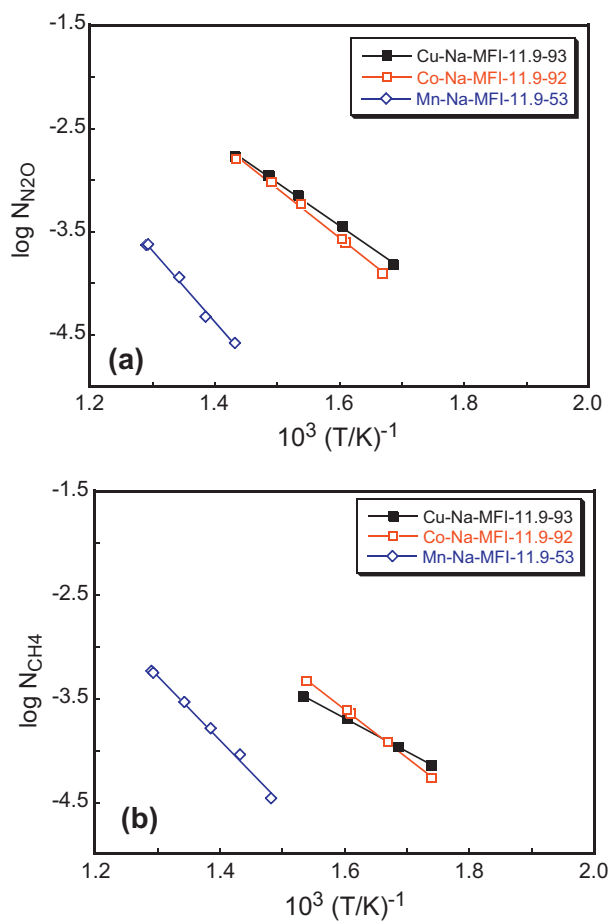


Fig. 8. Arrhenius plots for CH₄ + N₂O + O₂ (CH₄:N₂O:O₂ = 1000:4000:20,000), on Me-Na-MFI catalysts (Me = Cu, Co, or Mn), as indicated. Section a: log N_{N₂O} vs. 1/T (N_{N₂O}/molecules s⁻¹ atom⁻¹). Section b: log N_{CH₄} vs. 1/T (N_{CH₄}/molecules s⁻¹ atom⁻¹).

In CH₄ + O₂, N_{CH₄} (CH₄ molecules converted s⁻¹ atom⁻¹) on Co-Na-MFI nearly equalled that on Mn-Na-MFI, and it was substantially lower than that on Cu-Na-MFI (data not shown).

In the SCR of N₂O with CH₄, N_{N₂O} on Co-Na-MFI equalled that on Cu-Na-MFI, and it was much higher than that on Mn-Na-MFI (Fig. 8a). Analogously, in the same reaction, N_{CH₄} on Co-Na-MFI equalled that on Cu-Na-MFI, and was higher than that on Mn-Na-MFI (Fig. 8b).

4. Conclusions

To be active for the SCR of N₂O with CH₄, catalysts must be active for CH₄ + N₂O. Catalytic activity for CH₄ + N₂O does not

guarantee SCR activity, as shown for Mn-MFI, a catalyst that is active for CH₄ + N₂O but inactive for the SCR of N₂O with CH₄.

To be active in the SCR of N₂O with CH₄, catalysts do not necessarily need to possess high catalytic activity for N₂O decomposition. Notwithstanding their inactivity for N₂O decomposition, Cu-Na-MOR-9.2-20, and Cu-Na-MFI-11.9-22 are active for the SCR of N₂O with CH₄. Analogously, nor is low activity for CH₄ combustion with O₂ a prerequisite for catalyst to be active in the SCR of N₂O with CH₄. Notwithstanding their high activity for CH₄ + O₂, Cu-MOR and Cu-MFI are active for the SCR of N₂O with CH₄.

From a fundamental viewpoint, results clarify that on Cu-MOR, Cu-MFI, Co-MOR, and Co-MFI the SCR of N₂O with CH₄ consists of two nearly independent reactions: CH₄ + N₂O and CH₄ + O₂. Selectivity data show that CH₄ + N₂O prevails at high temperature, whereas CH₄ + O₂ prevails at low temperature. Based on these findings, we suggest that different oxygen species are active for CH₄ + O₂ and CH₄ + N₂O, most probably a molecular oxygen form for CH₄ + O₂, and a monoatomic oxygen form, arising from N₂O, for CH₄ + N₂O.

From an applied viewpoint, these results suggest that Co-MOR and Co-MFI, being highly active and selective for (i) the SCR of N₂O with CH₄ and (ii) the SCR of NO_x with CH₄ [14,15], are promising catalysts for the simultaneous SCR of N₂O and NO_x using CH₄ alone as the reducing agent.

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